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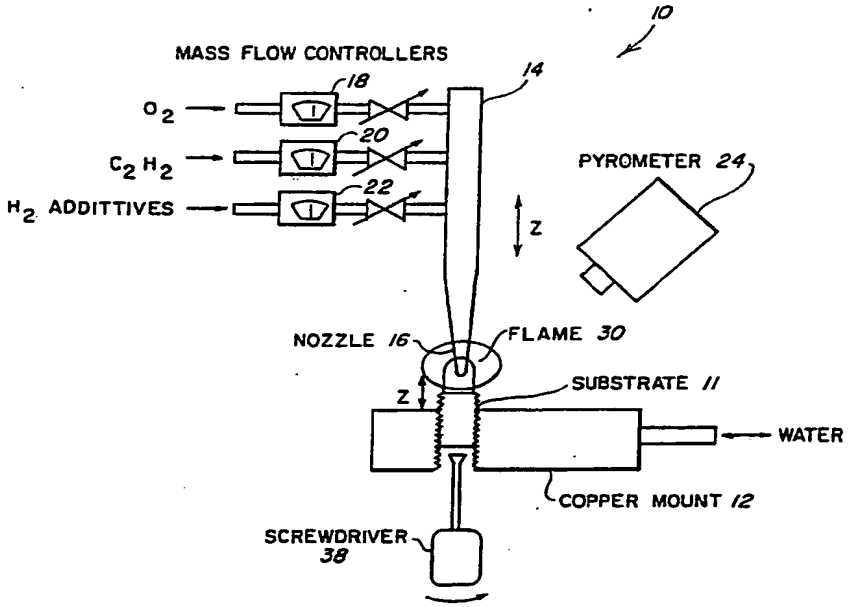

(57) Abstract

A method for synthesizing diamond which includes flowing together a gaseous carbon source and a gaseous hydrogen source to form an at least partially turbulent mixture. The at least partially turbulent mixture is excited to form an at least partially turbulent reactive species which is reacted to form a deposition species. A substrate is disposed in the deposition species while maintaining the substrate at a temperature for the deposition of diamond, thereby inducing deposition of diamond on the substrate.

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FLAME OR PLASMA SYNTHESIS OF DIAMOND UNDER TURBULENT AND TRANSITION FLOW CONDITIONS

Background of the Invention

Field of the Invention

This invention relates to a method for the chemical vapor deposition of high quality diamond on a substrate and the diamond so produced.

Description of the Prior Art

Diamond synthesis at low pressures (1-100 Torr) by chemical vapor deposition (CVD) using hydrocarbon gases mixed with H_2 has been the subject of expanding interest and investigation over the last two decades (see, for example, J.C. Angus and C.C. Hayman, Science 241 (1988) 913). Recently, the addition of oxygen-containing gases to the process was found to increase the maximum deposition rates of 1μm/h by an order of magnitude (see Y. Hirose and Y. Terasawa, Japan. J. Appl. Phys. 2 (1986) L.519 and J.A. Mucha, D.L. Flamm and D.E. Ibbotson, Program and Book of Abstracts, SDIO/1st-ONR Diamond Technology Initiative Symposium, 12-14 July, 1988, Crystal City, VA). In addition, the application of plasma jets running at high temperatures and flow rates to the CVD process has yield growth rates of up to 180 μm/h (see N. Koshino, K. Kurihara, M. Kawarada and K. Sasaki, Extended Book of Abstracts, MRS Conference on Diamond and Diamond-like Materials Synthesis, Reno, Nevada, April 1988, p. 434, and more recently 960μm/h by Ohtake et al., "Diamond Film Preparation by Arc Discharge Plasma Jet Chemical Vapor Deposition in the Methane Atmosphere", Journal of the Electrochemical Society, Vol. 137, No. 2, February 1990).

Hirose and Kondo have reported growth of diamond polycrystalline films using oxygen-acetylene flames with growth rates approaching 100 μm/h (see Y. Hirose and N. Kondo, Program

and Book of Abstracts, Japan Applied Physics 1988 Spring Meeting, March 29, 1988). Since then, Hirose and Mitsuizumi have reported the growth of diamond with acetylene, ethylene, methane, propane, methanol and ethanol gases burned in air when mixed with either hydrogen or oxygen (see Y. Hirose and M. Mitsuizumi, New Diamond 4, 34 (1988)). Growth was achieved on Si, SiC, Al_2O_3, W, WC, and Mo substrates in an oxygen-acetylene flame, and rates of 200 μm/hr for particle growth were reported. Subsequently, Hanssen et al. ("Diamond and non-diamond carbon synthesis in an oxygen-acetylene flame", accepted for publication in Thin Solid Films, June 1990, and the entirety of which is incorporated by reference herein) studied the effect of substrate position, gas flow ratio, and substrate temperature on diamond growth in an oxygen-acetylene flame, and observed growth on Si(100), Si(111), BN, Mo(100), Nb(100), TiC(100), Ta and Cu. Carrington et al. (Materials Letters, Vol. 7, No. 7,8, December 1988, pages 289 - 292, the entirety of which is incorporated herein by reference) have reported growth on Si(100) in oxygen-ethylene flame. More recently, Hirose et al. (ECS Proc. Vol 89-12, p. 80, May 7 - 12, the entirety of which is incorporated herein by reference) have reported on the growth of high quality diamond crystals in a flame at substrate temperatures of 500 to 700°C. The quality of these crystals was determined by their transparency under an optical microscope, and their Raman and x-ray diffraction spectra.

Notwithstanding these developments, there exists a need in the art for processes for producing diamonds of greater uniformity and higher quality.

Summary of the Invention

Therefore, it is an object of the invention to synthesize high quality diamond crystals and films uniformly over large areas, under controlled conditions.

This and other objects of the invention are accomplished by a method for synthesizing diamond which comprises flowing together a gaseous carbon source and a gaseous hydrogen source

to form a turbulent mixture. This turbulent mixture is excited to form a turbulent reactive species which is reacted to form a deposition species. A substrate is disposed in the deposition species while maintaining the substrate at a temperature for the deposition of diamond, thereby inducing deposition of diamond on the substrate.

Other features and advantages of the invention will be set forth in, or apparent from, the detailed description of preferred embodiments of the invention which follows.

Brief Description of the Drawings

Figure 1 illustrates in schematic form a combustion flame deposition apparatus for practicing the process according to the invention.

Figure 1A illustrates in detail the circled region of Figure 1.

Figure 2 illustrates typical operational regimes and limits for a torch burner, including the laminar regime, the turbulent regime and flashback and blow off limits.

Figure 3 shows a Raman spectra of a film grown according to the process of the invention.

Figure 4 shows the Raman spectra of diamond grown in a premixed, laminar oxygen-acetylene flame at substrate temperatures of 700 to 1200°C.

Figure 5 shows a Raman spectra for a natural type 1b diamond.

Figure 6 shows a Raman spectra for a natural type IIa diamond.

Figure 7 illustrates in schematic form a radio frequency plasma jet deposition apparatus for practicing the process according to the invention.

Figure 8 illustrates in schematic form a direct current plasma jet apparatus for practicing the process according to the invention.

Figure 9 is a photomicrograph of diamond grown in a turbulent flame according to the present invention.

Figure 10 shows the UV-visible and NIR hemispherical transmittance of an unpolished diamond film grown according to the present invention is and oxygen-acetylene flame.

Detailed Description of the Preferred Embodiments

The carbon sources which may be used in the chemical vapor deposition of diamond include but are not limited the following compounds which also function as sources for hydrogen:

Saturated hydrocarbons: methane, ethane, propane, butane, etc.

Unsaturated hydrocarbons: Ethylene, propylene, butylene, acetylene, etc.

Aromatic hydrocarbons: Benzene, toluene, xylene, cyclohexane, etc.

CHO compounds: Alcohols such as methanol, ethanol, propanol, butanol, ether group containing compounds.

Ketone group-containing compounds: Acetone, methyl ethyl ketone, diethyl ketone, 2,4-pentanedione, and 1'-butyronaphthone.

Esters: Methyl acetate, ethyl acetate, and isoamyl acetate.

Ketene group-containing compounds: Dimethyl ketene and phenyl ketene.

Acetyl group-containing compounds: Acetic acid, acetic anhydride, acetophenone, and biacetyl.

Aldehyde group-containing compounds: Formaldehyde, acetaldehyde and propionaldehyde.

Methylene group-containing compounds: Ketene and diazo methane.

Methyl group-containing compounds: t-Butyl peroxide, methyl hydroperoxide, and peracetic acid.

The compounds listed above can be used either singly or in combinations of two or more. Further, although the carbon and hydrogen sources listed above are the same gas, it is possible to use separate carbon and hydrogen sources in the turbulent mixture of gases, as well as diluents such as Argon, Xenon, etc.

Various types of chemical vapor deposition (CVD) techniques may be employed with the above carbon and hydrogen sources in practicing the invention. Such techniques include combustion flame deposition, radio frequency (RF) plasma jet deposition and direct current (DC) plasma jet deposition. For combustion flame deposition, a carbon source such as acetylene is preferable because it burns at a high temperature. However, when combustion flame deposition is used in combination with a microwave cavity or RF coil to excite the turbulent mixture of gases, it is possible to use carbon and hydrogen sources which burn at a lower temperature.

For deposition of large highly thermally conductive single diamond crystals, preferred carbon sources include isotopically enriched ^{12}C methane, acetylene or other hydrocarbons which yield diamond of a particularly high degree of purity.

The apparatus for synthesizing diamond using a turbulent or partially turbulent combustion flame technique typically includes a commercial oxygen-acetylene brazing torch, a mass flow control system, a supply of oxygen and acetylene, a substrate (e.g. Si, Mo, TiC, diamond, etc.), a device for controlling the temperature of the substrate, and a thermocouple or pyrometer for measuring the temperature of the substrate. A typical apparatus 10 incorporating these elements is illustrated in schematic form in Figure 1.

In apparatus 10, a substrate 11 is mounted on a water-cooled copper block mount 12. An oxygen-acetylene welding torch 14 is fitted with a brazing or cutting nozzle 16 in order to deposit diamond. A suitable welding torch has a size #4 tip. Mass flow controllers 18, 20 and 22 are used to measure gas flow rates and ratios. Welder's grade or high purity acetylene and 99.99% purity grade oxygen are preferably used as source gases. An activated charcoal trap or other suitable device may be used to remove acetone from the acetylene. The torch 14 is preferably mounted on an xyz translation stage for accurate and repeatable positioning. A two-color near-infrared pyrometer 24 is used to monitor substrate temperatures, T, which vary from about 300°C to 1200°C. The pyrometer can be calibrated with a chromel/alumel thermocouple attached to a Si

substrate heated in a tube furnace up to 1000°C. The temperature measuring device or pyrometer 24 should be insensitive to the flame emission. The temperature of the substrate 11 is adjusted by rotating a screwdriver 38 which may be used to vary the degree of insertion of the substrate 11 in the copper mount 12.

A stationary oxygen-acetylene flame 30 is illustrated in Figure 1A. Three regions are shown: an inside cone 32 bounded by the O_2-C_2H_2 flame front, an incomplete combustion region or C_2H_2 feather 34 where excess C_2H_2 burns with O_2, which diffuses into the flame from the surrounding air (the size of the feather is dependent on the gas flow ratio and only appears when the torch is run C_2H_2 rich); and outside flame 36 where the CO and H_2 produced on the inside cone burns to produce CO_2 and H_2O. The flame temperature at the inner cone 32 varies with the ratio, R, of O_2 to C_2H_2 gas flow from 3162°C for a flame with R= 1.5, to 2960°C for R = 0.8.

In the process of the invention the torch is operated in a turbulent, rather than laminar mode. The different operational modes of a torch burner are shown in Figure 2. The laminar and turbulent regimes are separated by a curve defined by the Reynolds number being equal to ~1200-2000. The regimes are bounded from above by the blow-off limit and from below by the flashback limit. The transition from laminar to turbulent flow usually occurs for Reynolds (Re) numbers of about 2200 (see R.B. Bird, W.E. Stewart, E.N. Lightfoot, "Transport Phenomena", pp. 153-156, John Wiley, 1960). For the purposes of the invention, the Reynolds number is defined as:

$$Re=\langle v\rangle \rho d/\mu$$

where $\langle v\rangle$ is the average velocity, ρ is the density, d is the tube diameter of the torch, and μ is the viscosity. For Re < 1200, the flow is always laminar. In the transition region, 1200 < Re < 2200, small random flow fluctuations tend to be damped out, but the flow is unstable to larger fluctuations. Abrupt switches from laminar to turbulent behavior are thus possible in this transition region.

While for laminar flames, the flame front is thin and conical or bell shaped, when a flame becomes turbulent, the center of the flame front blurs, but remains steady. This generally occurs when the Re for the flame is near 2200. The flame noise also begins to increase. With increased turbulence, the whole volume in which the primary combustion occurs becomes very thick and blurred; this region is called the "flame brush".

The temperature of the substrate may be controlled in a variety of ways including clamping the substrate to a heat sink and flowing cool gas over the bottom of the substrate or the apparatus on which it is mounted. In a preferred embodiment, the substrate is machined into a threaded rod, and the penetration of the rod into a water cooled metal mount is used to control the temperature. The threaded rod is typically made of Mo, but coatings (e.g. Si, TiC, Ta, etc.) can be applied to the surface of the rod, or other materials (eg. diamond, BN, etc.) can be brazed or attached to the Mo.

In a combustion flame deposition, turbulence in the gas mixture can be produced by using diffusion or surface mixed flame techniques by preventing pre-mixing the fuel and oxidizer, usually oxygen, and mixing these components of the flame only when they arrive at the surface of the burner.

Turbulence in the gaseous mixture may also be generated using a flat flame burner operated with a sufficiently high Reynolds number. Types of flat flame burners include microtube, fritted plug, porous plug, etc., burners. Co-axial sheath flames may be needed to stabilize turbulent flames on flat flame burners. Sheath gas feeder systems can also be used to exclude nitrogen and oxygen from deposition processes in open air.

The mixture of gases can be made turbulent in CVD techniques other than combustion flame deposition. Some of these techniques include using a radio frequency (RF) plasma jet or a direct current (DC) plasma jet, so-called "plasma spraying guns". While the O_2 is not normally used to a great extent in plasma jet depositions, the inclusion of O_2 via the feedstock gases or via entrainment of room air enhances the

effect of turbulence in the plasma jet depositions according to the present invention and provides diamond of improved quality.

An apparatus for using an RF plasma jet is illustrated in Figure 7. The apparatus is similar to that for a combustion flame but includes a tube 40, preferably made of quartz, in place of the combustion flame nozzle. A copper RF coil 42 is wound around the tube 40 to generate RF waves which excite the gases in the tube 40 to form a plasma region 44 which deposits diamond on substrate 11. While the plasma region 44 is shown as existing outside the tube 40, in fact, the plasma region extends inside of RF tube 42. A temperature measuring device 124 is used to monitor the temperature of the plasma region 44, and of the substrate.

Detailed descriptions of RF plasma jet processes which may be modified to be used with the method of the invention are described in Matsumoto et al., "Synthesis of diamond films in a rf induction thermal plasma", Appl. Phys. Lett. 51 (10), 7 September 1987 and M.A. Capelli, et al., "High Growth Rate Diamond Synthesis in a Large Area Atmospheric Pressure Inductively Coupled Plasma", preprint to be published in J. Matls. Research, Nov. 1990, the entire contents and disclosures of which are hereby incorporated by reference.

An apparatus for using a DC plasma jet is illustrated in Figure 8. The apparatus is similar to that for an RF plasma jet but includes a nozzle 50 having an electrode 52 therein in place of RF tube 42. The electrode 52 is connected to a power source (not shown) and is oppositely charged relative to the nozzle 50 so that there is a discharge between the electrode 52 and the nozzle 50. This discharge causes the excitation of the gases in the nozzle 50 and the formation of a plasma region 54 which deposits diamond on the substrate 11. Generally, the diameter of nozzle 50 for a DC plasma jet apparatus is larger than the diameter of the nozzle for a combustion flame apparatus.

Detailed descriptions of DC plasma jet processes which may be modified to be used with the method of the invention are described in Ohtake et al. cited above and in Klocek et al.,

"CVD diamond growth by dc plasma torch", SPIE Proceedings Vol. 1325, 1990, the entire contents and disclosures of which are hereby incorporated by reference.

Turbulence can also be produced by aligning multiple gas streams so they interact to cause turbulence, by using a gas flow line having a roughened surface, or by incorporating a wire mesh in the gas flow lines which supply any of the gases.

Another technique which may be employed to create a turbulent flame is to use a linear burner run in either a premixed or a diffusion mode, with a sufficiently high Reynolds number. Linear burners have a rectangular or elongated flame cross section and are useful for continuous deposition processes. They are usually of the microtube type. In the case of a diffusion flame, the fuel and oxidizer are usually diluted with a rare gas such as argon, in order to prevent localized sooting.

The method of the invention may be practiced under various pressures, but preferably the combustion flame deposition or plasma deposition of diamond is performed in a low pressure chamber. CVD is preferably performed in a chamber near or below atmospheric pressure, because lower pressures expand the size of the plasma or combustion zone suitable for growing diamond and because low pressure chambers permit one to exclude nitrogen from the growth environment. The substrate used in the method of the invention may be any of the materials conventionally used for synthesis by low-pressure CVD. As concrete examples of the substrate, there may be cited shaped articles such as Si wafer, sintered SiC, granular SiC, SiN, W, WC, Mo, TiC, TiN, thermet, ultra-hard special tool steels, special tool steels, high-speed steel, and natural or synthetic diamond.

In order to coat large areas of a substrate, the reacted turbulent gases may be passed over the surface of a stationary substrate or the substrate may pass over a stationary reactive turbulent gas stream.

Preferably, the substrate is held at a temperature of about 300-1700°C. Most preferably, th a diamond film is deposited onto a substrate held at 700-1100°C, a temperature

at which the diamond surface remains hydrogen terminated. If graphite nucleation is impeded, diamond growth can be observed at higher temperatures (e.g. 1100-1700°C) on Au-Ta braze coatings and on diamond seed crystals. The upper temperature limit for diamond-on-diamond growth is determined by the desorption of hydrogen and the stability of the diamond crystal, and may exceed 1700°C if sufficient hydrogen flux is available.

The Raman spectra of a diamond film grown in a turbulent flame using the apparatus of Figure 1 is shown in Figure 3. In this spectra, there is a featureless fluorescence background and an extremely sharp peak due to diamond at 1332 cm^{-1}. For comparison, the Raman spectra of 5 samples grown in a laminar oxygen-acetylene flame at temperatures ranging from 700-1200°C is shown in Figure 4. It should be noted that the presence of peaks due to amorphous carbon (broad peak around 1500 cm^{-1}) at most temperatures, and graphite (peaks at 1350 cm^{-1} and 1580 cm^{-1}) at higher temperatures. A high fluorescence background is also observed at all temperatures. As a further comparison, a Raman spectra for a natural type 1b diamond (nitrogen in the 100-1000 ppm levels) is shown in Figure 5, and that of a type IIa diamond (no nitrogen) in Figure 6.

Having described the invention, the following examples are given to illustrate specific applications of the invention including the best mode now known to perform the invention. These specific examples are not intended to limit the scope of the invention described in this application.

EXAMPLES

The apparatus used for the carbon growth consisted of a commercial oxygen-acetylene brazing torch, fed by a gas mass flow control system, and a water cooled copper substrate mount. A two-color IR pyrometer (which measures 2.2 and 2.4 μm IR radiation) was used to monitor the substrate temperature during growth. The arrangement of these components is shown in Figure 1.

High purity oxygen (99.99%) and acetylene (99.6%) were used as source gases, with the acetylene passed through an activated charcoal trap to remove residual acetone. For the growths performed, the ratio (R_f), of the flow rate of oxygen to the flow rate of acetylene was kept relatively constant an near 1.0-1.1. R_f was chosen so that a small excess acetylene feather existed just beyond the primary flame front. The exact value of R_f depends on the efficiency of mixing in the torch employed, the rate of room air entrainment, and the gas correction factors used in the mass flow controllers. Premixed oxygen-acetylene flames generated with a #4 brazing tip (1.85 mm tube diameter). The oxygen/acetylene flow ratio was kept constant at approximately 1.1 and the total flow was varied from 5-20 slm. At 5 slm, the flame is conical with a somewhat laminar flow. For a number 4 tip, the flame front zone broadens as total flow is increased to 10 slm, and develops a rounded end and very broad flame front at 20 slm.

The viscosity of a mixture of oxygen and acetylene was calculated with the semiempirical formula of Wilke, J. Chem. Phys. 18, 517 (1950). Assuming a temperature of 500 K and a 1:1 mixture of oxygen:acetylene, the viscosity of the gases in the torch near the flame from was estimated as 2.2×10^{-4} gm·cm/s. For the condition corresponding to the flames at 5, 10 and 20 slm, the Reynolds numbers were calculated as 1600, 2800 and 6600, respectively.

The Raman spectra of a polycrystalline diamond film grown at T_s=900°C is shown in Figure 3, which was discussed above. Crystals grown under proper conditions in a turbulent flame are frequently transparent enough to allow one to image the Mo

substrate through individual crystals with an optical microscope; thin films are whitish in color and sufficiently transparent to read newsprint through. A scanning electron micrograph (Figure 9) shows that the surface of the film is composed of well facetted twinned crystallite with very little secondary nucleation on the crystal faces.

The UV, visible and NIR hemispherical transmittance of a diamond film synthesized in a turbulent flame is shown in Figure 10. Note the high transmittance thought the UV visible and NIR. the slightly higher transmittance for the rough side of the film, compared to the smooth substrate side, has been observed before and has been ascribed to total internal reflection effects.

While the FWHM of synthetic diamond produced according to the present invention has not yet been determined, it is believed that diamonds made according to the present invention have a FWHM near that of natural diamond (2.2 cm^{-1}), for example, less than 4 cm^{-1}, typically less than 3.7 cm^{-1} and perhaps less than 3.5 cm^{-1} or 3 cm^{-1}. Also, microcrystals according to the present invention are microscopically transparent or essentially so. Additionally, it may be possible, using the method of the present invention, to produce macroscopic crystals.

It will be understood by those skilled in the art that although the invention has been described relative to exemplary embodiments thereof, variations and modifications can be effected in these embodiments without departing from the scope and spirit of the invention.

Claims

What is claimed is:

1. A method for synthesizing diamond comprising the steps of:

flowing together a gaseous carbon source and a gaseous hydrogen source to form an at least partially turbulent mixture;

exciting the at least partially turbulent mixture to form an at least partially turbulent reactive species;

reacting the reactive species to form a deposition species;

disposing a substrate for deposition of diamond in the deposition species; and

maintaining the substrate at a temperature for the deposition of diamond, thereby inducing deposition of diamond on the substrate.

2. The method of claim 1, wherein the gas flow in the reactive species has a Reynolds number of at least about 1200.

3. The method of claim 1, wherein the gas flow in the reactive species has a Reynolds number of at least about 2200.

4. The method of claim 1, further comprising flowing together an oxidizer with the carbon source and the hydrogen source to form the at least partially turbulent mixture, and the reactive species comprises an at least partially turbulent combustion flame formed by flowing the at least partially turbulent mixture in a burner.

5. The method of claim 4, wherein the at least partially turbulent combustion flame has a boundary layer at the substrate which is about 1 to about 10 μm thick.

6. The method of claim 4, wherein the at least partially turbulent combustion flame is a diffusion flame and is

controlled by mixing the carbon source and the oxidizer at the surface of the burner.

7. The method of claim 4, wherein the at least partially turbulent combustion flame is generated by a flat flame burner selected from the group consisting of microtube burners, fritted plug burners, and porous plug burners.

8. The method of claim 4, wherein the carbon source and oxidizer flow to the at least partially turbulent mixture in multiple interacting gas streams and the at least partially turbulent mixture is formed by aligning the streams together.

9. The method of claim 4, wherein the carbon source and oxidizer are fed into the at least partially turbulent mixture in gas streams and the gas streams pass over roughened surfaces to cause turbulence in the at least partially turbulent combustion flame.

10. The method of claim 4, wherein the carbon source material and the oxidizer are mixed to form a single mixed gas stream and the at least partially turbulent mixture is formed by causing the mixed gas stream to pass through a wire mesh.

11. The method of claim 1, wherein the at least partially turbulent mixture is excited by a radio frequency plasma jet to form an at least partially turbulent reactive species.

12. The method of claim 11, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the at least partially turbulent mixture is formed by aligning the streams of the carbon source and the hydrogen source to interact and cause turbulence.

13. The method of claim 11, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass over roughened

surfaces to cause turbulence in the at least partially turbulent mixture.

14. The method of claim 11 wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass through a wire mesh to cause turbulence in the at least partially turbulent mixture.

15. The method of claim 1, wherein the at least partially turbulent mixture is excited by a DC plasma jet to form an at least partially turbulent reactive species.

16. The method of claim 15, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the at least partially turbulent mixture is formed by aligning the streams to interact and cause turbulence.

17. The method of claim 15, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass over roughened surfaces to cause turbulence in the at least partially turbulent mixture.

18. The method of claim 15, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass through a wire mesh to cause turbulence in the at least partially turbulent mixture.

19. The method of claim 1, wherein the substrate comprises a diamond crystal and the substrate is maintained at a temperature between about 300 and 1700°C.

20. The method of claim 19, wherein the carbon source is a hydrocarbon isotopically enriched with ^{12}C.

21. The method of claim 1, wherein the substrate is maintained at a temperature at which the diamond surface remains hydrogen terminated.

22. The method of claim 1, wherein the reactive species is under a less than atmospheric pressure.

23. Diamond produced according to the method of claim 1.

24. Diamond produced according the method of claim 4.

25. Diamond produced according to the method of claim 11.

26. Diamond produced according to the method of claim 15.

27. Diamond produced according to the method of claim 19.

28. A synthetic diamond which is essentially transparent and has an FWHM of less than 3.7.

AMENDED CLAIMS

[received by the International Bureau on 10 March 1992(10.03.92); origi :l claim 22 cancelled; original claims 1,4,11,15 and 28 amended; new claim 29 added; other claims unchanged (4 pages)]

1. A method for synthesizing diamond comprising the steps of:

flowing together a gaseous carbon source and a gaseous hydrogen source to form a gaseous flow of an at least partially turbulent gaseous mixture;

exciting the at least partially turbulent gaseous mixture to form an at least partially turbulent gaseous flow of a reactive species;

reacting the at least partially turbulent gaseous flow of said reactive species to form an at least partially turbulent gaseous flow of a deposition species;

mounting a substrate for deposition of diamond to a mount including means for cooling said substrate independently of the temperature of said at least partially turbulent gaseous flow of said deposition species;

disposing said mounted substrate in the at least partially turbulent gaseous flow of said deposition species; and

maintaining the substrate at a temperature for the deposition of diamond, thereby inducing deposition of diamond on they substrate;

wherein an at least partially turbulent flow is defined as a flow which is under turbulent flow conditions or which is under transition zone flow conditions.

2. The method of claim 1, wherein the gas flow in the reactive species has a Reynolds number of at least about 1200.

3. The method of claim 1, wherein the gas flow in the reactive species has a Reynolds number of at least about 2200.

4. The method of claim 1, further comprising flowing together an oxidizer with the carbon source and the hydrogen source to form the at least partially turbulent mixture, and the reactive species comprises an at least partially turbulent combustion flame formed by flowing the at least partially turbulent

mixture in a burner, wherein said deposition of diamond is conducted at about atmospheric pressure.

5. The method of claim 4, wherein the at least partially turbulent combustion flame has a boundary layer at the substrate which is about 1 to about 10 μm thick.

6. The method of claim 4, wherein the at least partially turbulent combustion flame is a diffusion flame and is controlled by mixing the carbon source and the oxidizer at the surface of the burner.

7. The method of claim 4, wherein the at least partially turbulent combustion flame is generated by a flat flame burner selected from the group consisting of microtube burners, fritted plug burners, and porous plug burners.

8. The method of claim 4, wherein the carbon source and oxidizer flow to the at least partially turbulent mixture in multiple interacting gas streams and the at least partially turbulent mixture is formed by aligning the streams together.

9. The method of claim 4, wherein the carbon source and oxidizer are fed into the at least partially turbulent mixture in gas streams and the gas streams pass over roughened surfaces to cause turbulence in the at least partially turbulent combustion flame.

10. The method of claim 4, wherein the carbon source material and the oxidizer are mixed to form a single mixed gas stream and the at least partially turbulent mixture is formed by causing the mixed gas stream to pass through a wire mesh.

11. The method of claim 1, wherein the at least partially turbulent mixture is excited by a DC plasma jet to form an at least partially turbulent reactive species, and wherein said deposition occurs at about atmospheric pressure.

12. The method of claim 11, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the at least partially turbulent mixture is formed by aligning the streams of the carbon source and the hydrogen source to interact and cause turbulence.

13. The method of claim 11, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass over roughened surfaces to cause turbulence in the at least partially turbulent mixture.

14. The method of claim 11 wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass through a wire mesh to cause turbulence in the at least partially turbulent mixture.

15. The method of claim 1, wherein the at least partially turbulent mixture is excited by a DC plasma jet to form an at least partially turbulent reactive species, and wherein said deposition occurs at about atmospheric pressure.

16. The method of claim 15, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the at least partially turbulent mixture is formed by aligning the streams to interact and cause turbulence.

17. The method of claim 15, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass over roughened surfaces to cause turbulence in the at least partially turbulent mixture.

18. The method of claim 15, wherein the carbon source and hydrogen source flow to the at least partially turbulent mixture in gas streams and the gas streams pass through a wire

mesh to cause turbulence in the at least partially turbulent mixture.

19. The method of claim 1, wherein the substrate comprises a diamond crystal and the substrate is maintained at a temperature between about 300 and 1700°C.

20. The method of claim 19, wherein the carbon source is a hydrocarbon isotopically enriched with ^{12}C.

21. The method of claim 1, wherein the substrate is maintained at a temperature at which the diamond surface remains hydrogen terminated.

23. A synthetic diamond which is essentially transparent and has a Full Width at Half Maximum of less than 3.7 cm^{-1}.

24. Diamond produced according the method of claim 4.

25. Diamond produced according to the method of claim 11.

26. Diamond produced according to the method of claim 15.

27. Diamond produced according to the method of claim 19.

28. A synthetic diamond which is essentially transparent and has an FWHM of less than 3.7.

29. A synthetic diamond which is essentially transparent and has a Full Width at Half Maximum of less than 3.5 cm^{-1}.

STATEMENT UNDER ARTICLE 19

The claims have been revised to recite mounting of the substrate to a mount having a means for cooling the temperature of the substrate. Lemelson never suggests control of the substrate temperature independent of the temperature of the gases. Thus, Lemelson must control the temperature of the gases to within a range that provides substrate temperatures suitable for diamond deposition. The gas temperature can be controlled by altering the composition of the gas, to control the reaction rate and the subsequent generation of heat, or by altering the amount of microwave or other energy applied to the plasma. Both methods severely restrict the operating conditions used and can prevent optimum diamond deposition. Because the method of the invention controls substrate temperatures by means which operate independently of the gas temperatures, the claimed method permits diamond growth at high gas temperatures, such as 2960°C to 3162°C.

The claims have also been revised to recite that the at least partially turbulent flows are gaseous, unlike the fluidized beds disclosed by Lemelson. In these fluidized beds, if any turbulent flow inherently occurs, that flow is the flow of the fluidized bed, not the gaseous flow of the precursors. The holes within the grills of the Lemelson gas supply means can provide either laminar or turbulent jets of gaseous precursors, depending upon how they are operated, in particular the velocities at which they operate.

As stated above, the claims have been revised to recite mounting of the substrate to a mount having a means for cooling the temperature of the substrate. Goforth states, at col. 7, lines 32 through 39:

> Both the temperature of the substrate plates 28 and 30 and the intensity of the plasma within the reaction tube 20, particularly within the region between the plates 28 and 30, is maintained by the microwave energy provided by the microwave energy source 14. Sufficient energy is supplied to establish a uniform temperature therein of about 900°C to about 1050°C.

Thus, Goforth teaches away from controlling the temperature of the substrate independently of the temperature of the deposition gases.

With special regard to claims 4, 11 and 15, which have been revised to recite diamond deposition at about atmospheric pressure, microwave CVD at the relatively low pressures (4 to 10 torr) used by Goforth (col. 2, line 28) vastly differs from flame and plasma torch deposition at about atmospheric pressure (atmospheric pressure processes are considered low pressure diamond growth processes, since the standard diamond growth techniques had been conducted at high pressures; the pressure used by Goforth would be considered to be relatively vacuum conditions in the diamond growth field). Goforth also requires a deposition atmosphere at about 900 to 1000°C. In flame and plasma torch techniques, the deposition species are typically at over 2900°C while the substrate is maintained at about 300°C to 1700°C. CVD reactors such as those described by Goforth only achieve diamond growth rates of about 0.1 to 1 μm/hr, whereas flame and plasma torch deposition systems can achieve growth rates of several hundred μm/hr. In addition, plasma torches operated at or near atmospheric pressure generate a thermal plasma (i.e., in thermal equilibrium) which can be modelled, whereas low pressure microwave CVD systems produce a non-equilibrium plasma which is very difficult to model and understand.

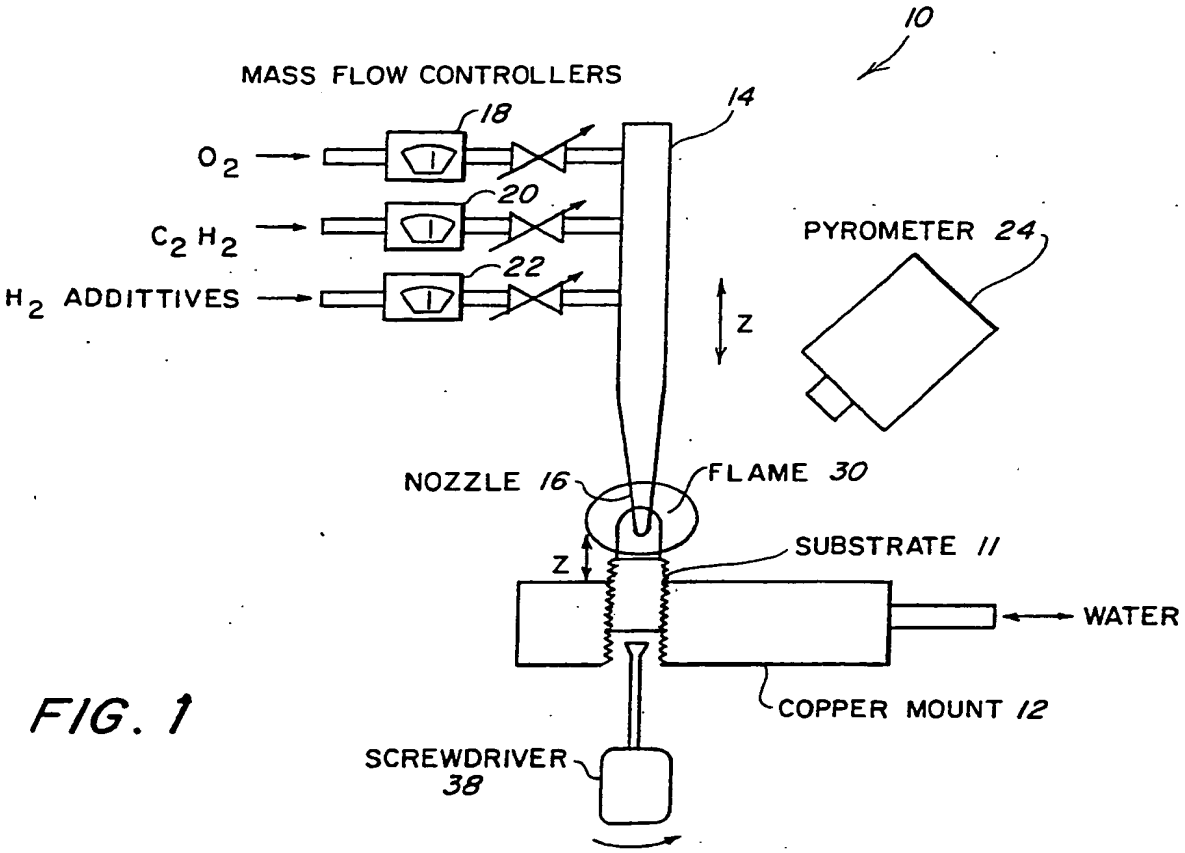
10
MASS FLOW CONTROLLERS
18
14
O_2
20
C_2H_2
22
H_2 ADDITTIVES
Z
PYROMETER 24
NOZZLE 16
FLAME 30
Z
SUBSTRATE 11
WATER
COPPER MOUNT 12
SCREWDRIVER
38

FIG. 1

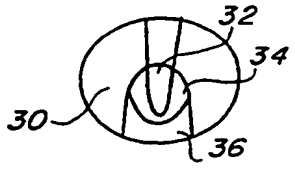
32
34
30
36

FIG. 1A

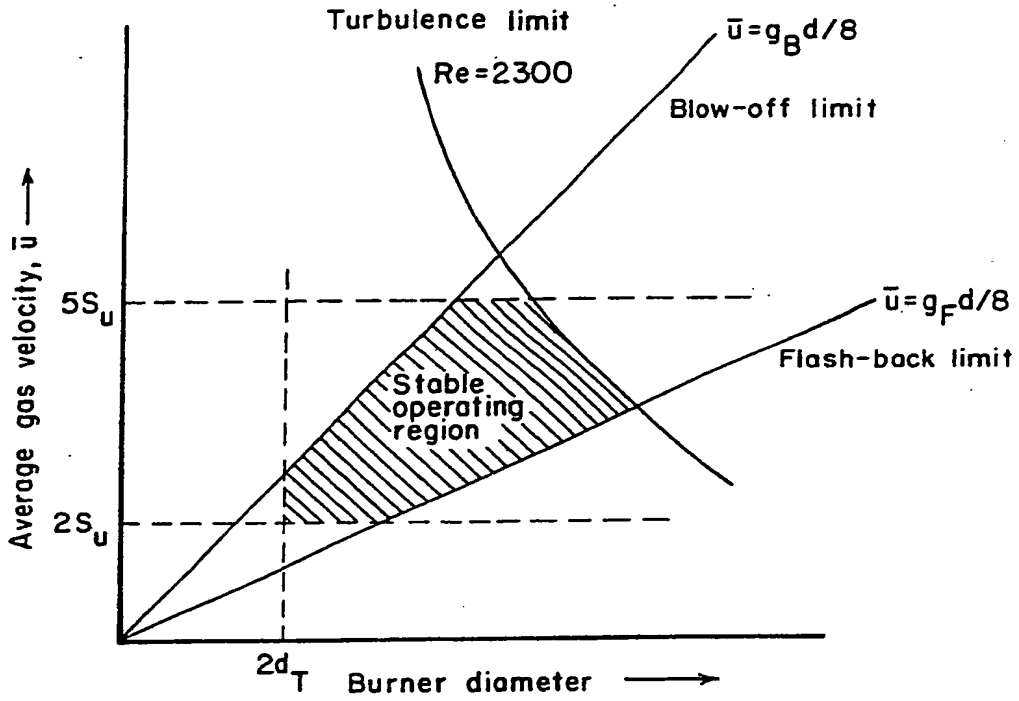
Turbulence limit
Re=2300
$\bar{u}=g_B d/8$
Blow-off limit
$\bar{u}=g_F d/8$
Flash-back limit
Stable operating region
Average gas velocity, $\bar{u}$
$5S_u$
$2S_u$
$2d_T$
Burner diameter

FIG. 2

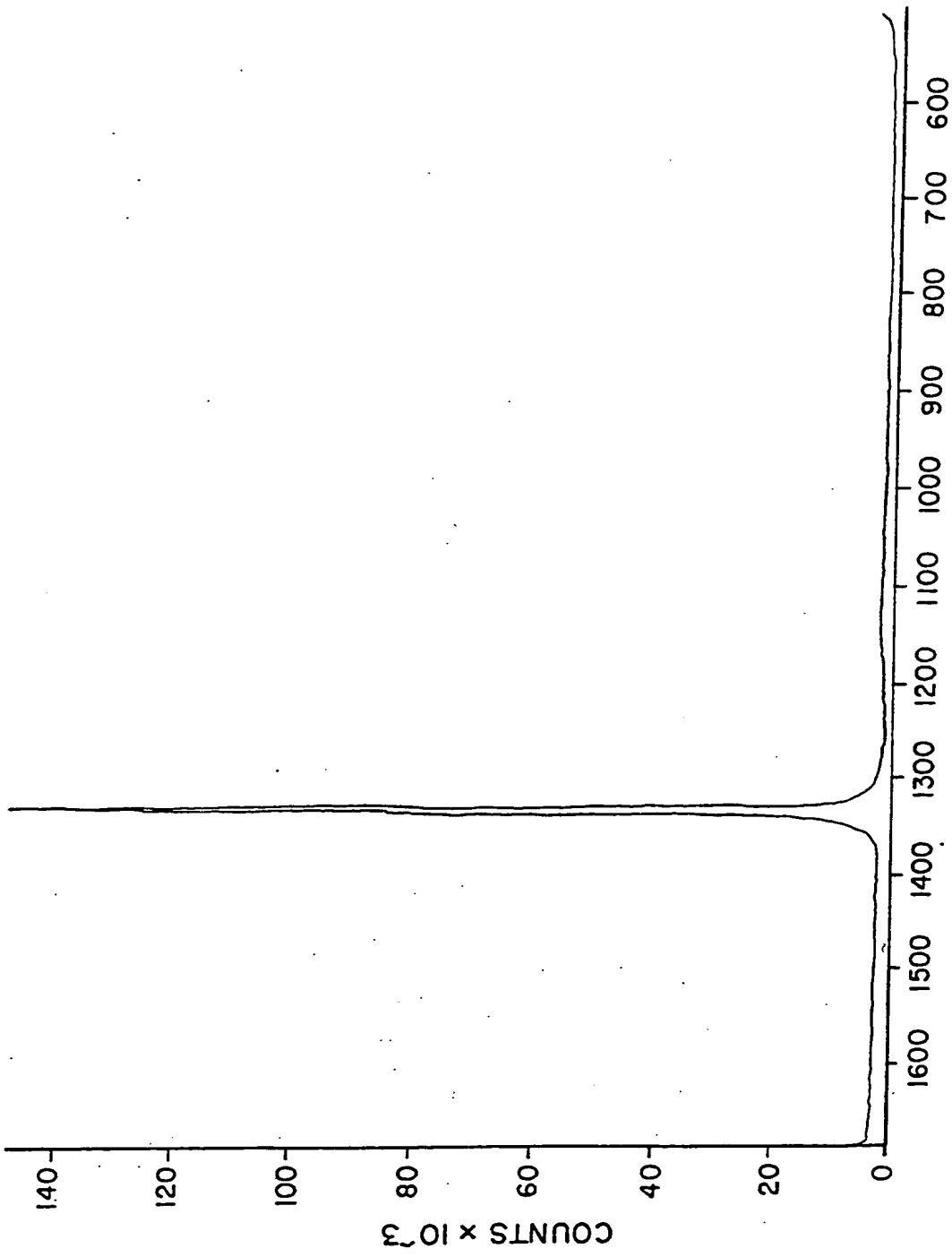
COUNTS x 10^3
0
20
40
60
80
100
120
140
600
700
800
900
1000
1100
1200
1300
1400
1500
1600

FIG. 3

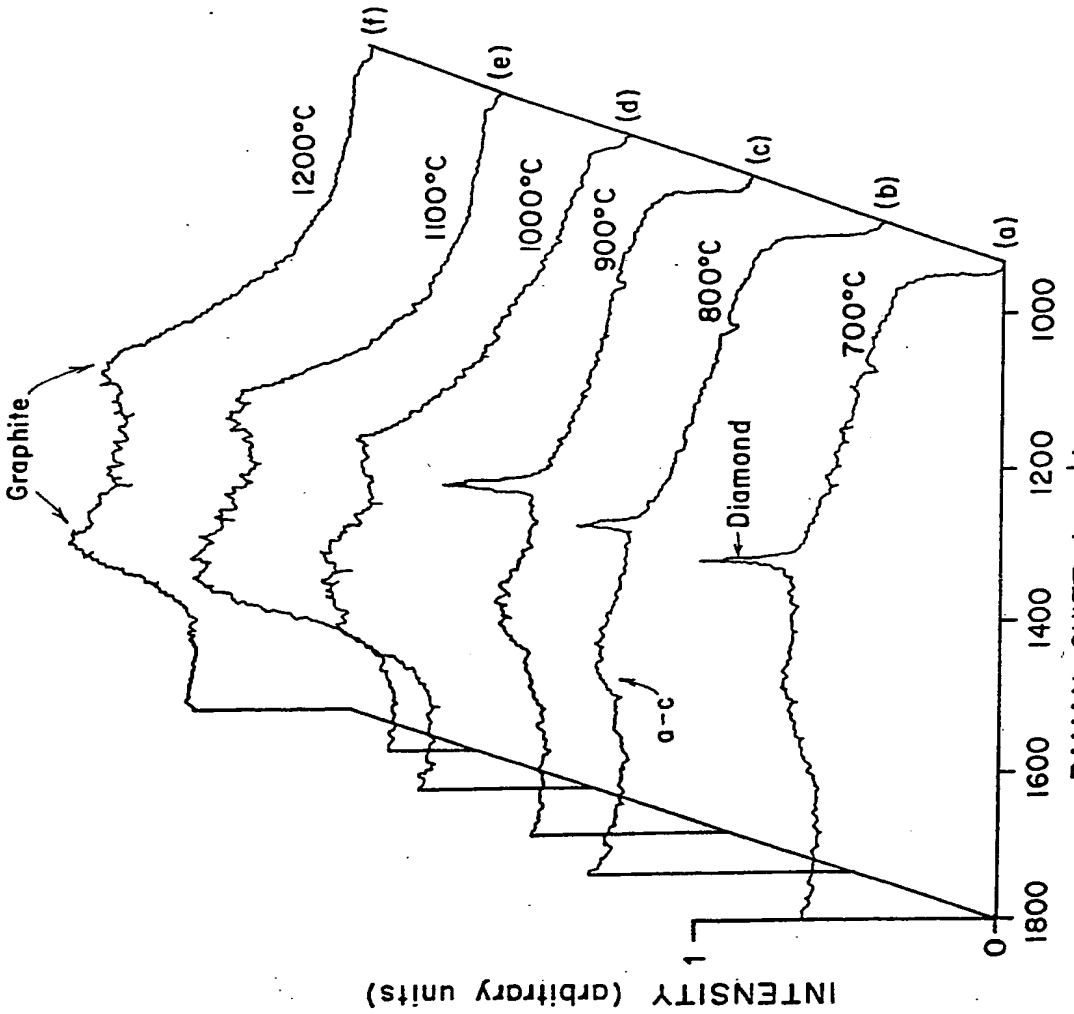
(f)
(e)
(d)
(c)
(b)
(a)
1200°C
1100°C
1000°C
900°C
800°C
700°C
Graphite
Diamond
a-c
0
1
INTENSITY (arbitrary units)
1000
1200
1400
1600
1800
RAMAN SHIFT (cm⁻¹)

FIG. 4

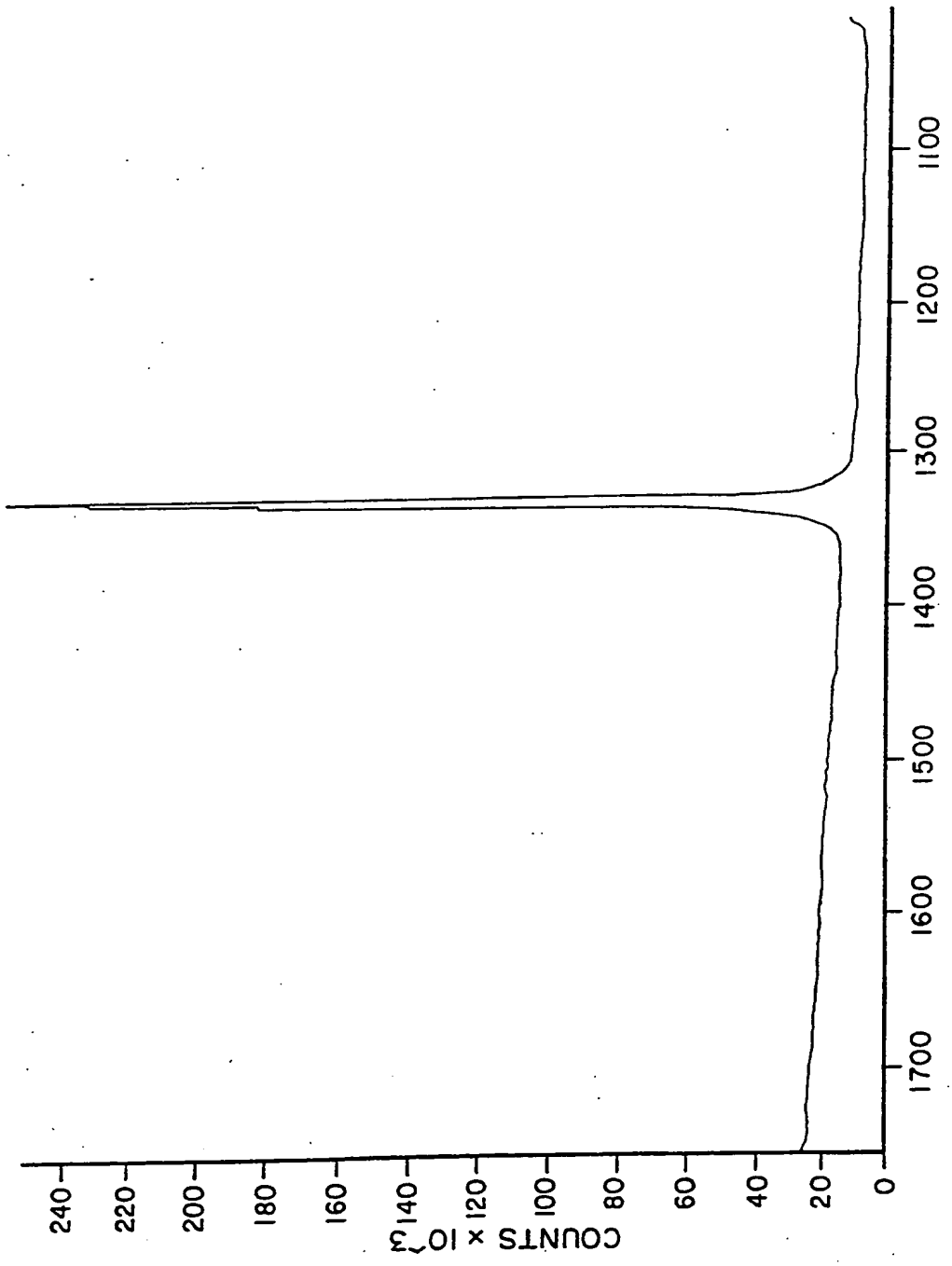
COUNTS x 10^3
0
20
40
60
80
100
120
140
160
180
200
220
240
1100
1200
1300
1400
1500
1600
1700

FIG. 5

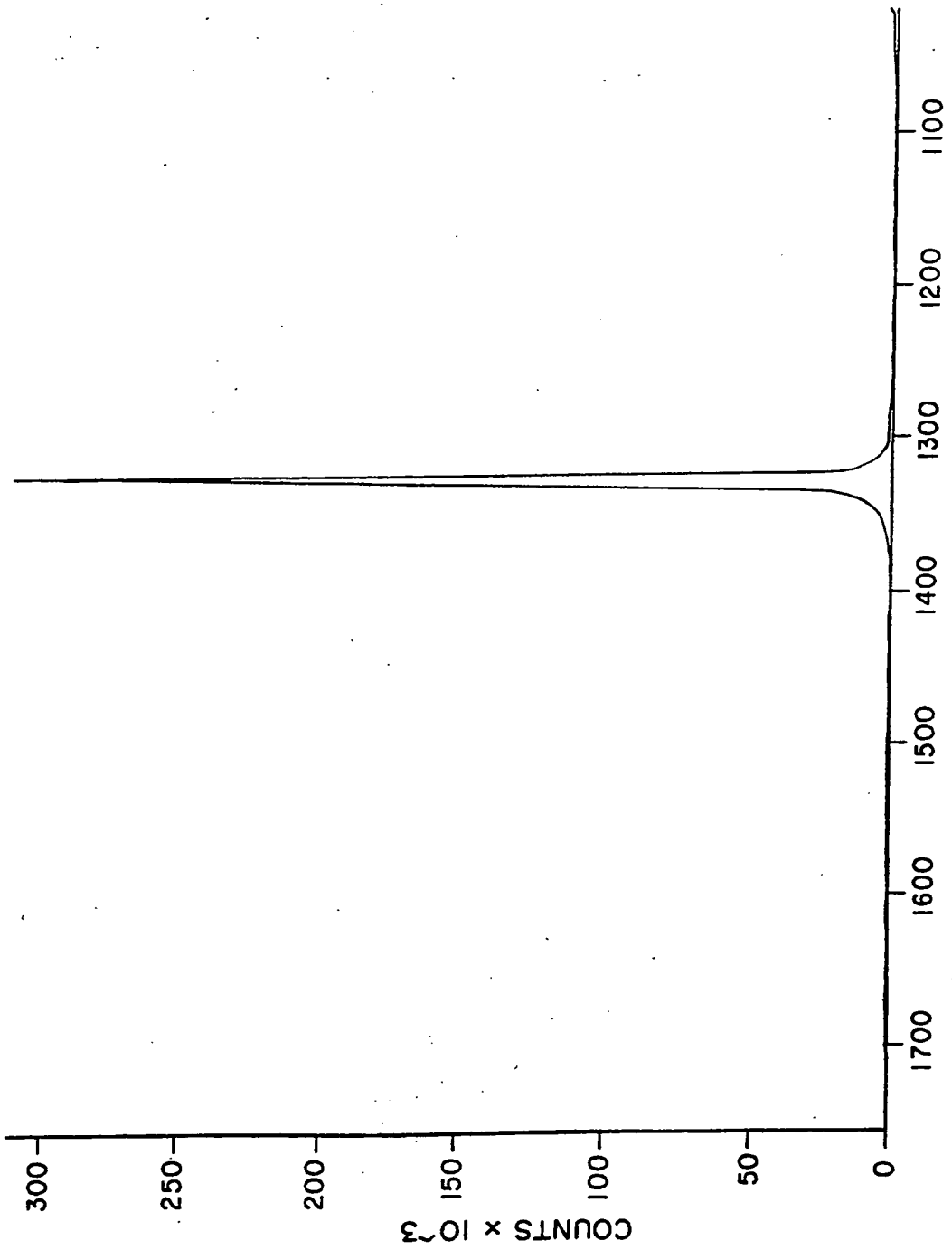
COUNTS x 10^3
300
250
200
150
100
50
0
1100
1200
1300
1400
1500
1600
1700

FIG. 6

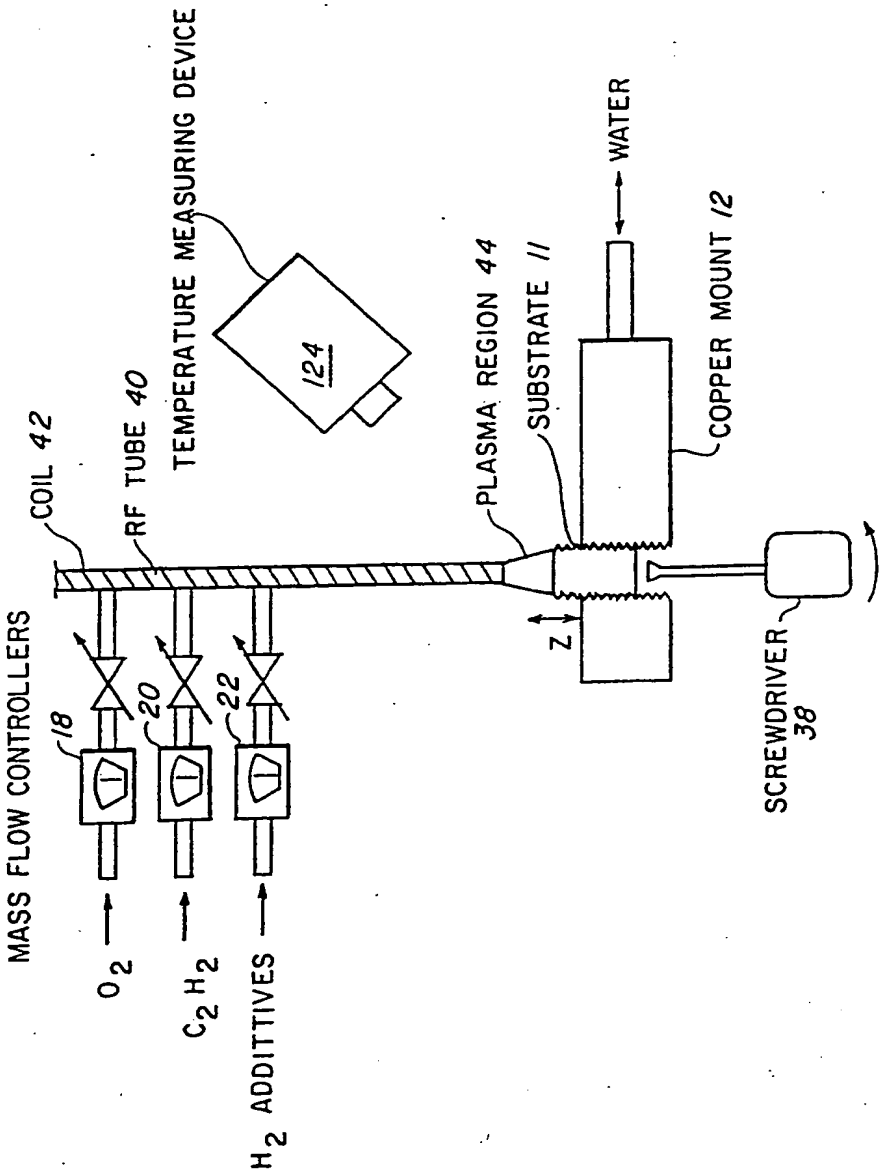
MASS FLOW CONTROLLERS
18
20
22
O_2
C_2H_2
H_2 ADDITIVES
COIL 42
RF TUBE 40
TEMPERATURE MEASURING DEVICE
124
PLASMA REGION 44
SUBSTRATE 11
WATER
COPPER MOUNT 12
Z
SCREWDRIVER 38

FIG. 7

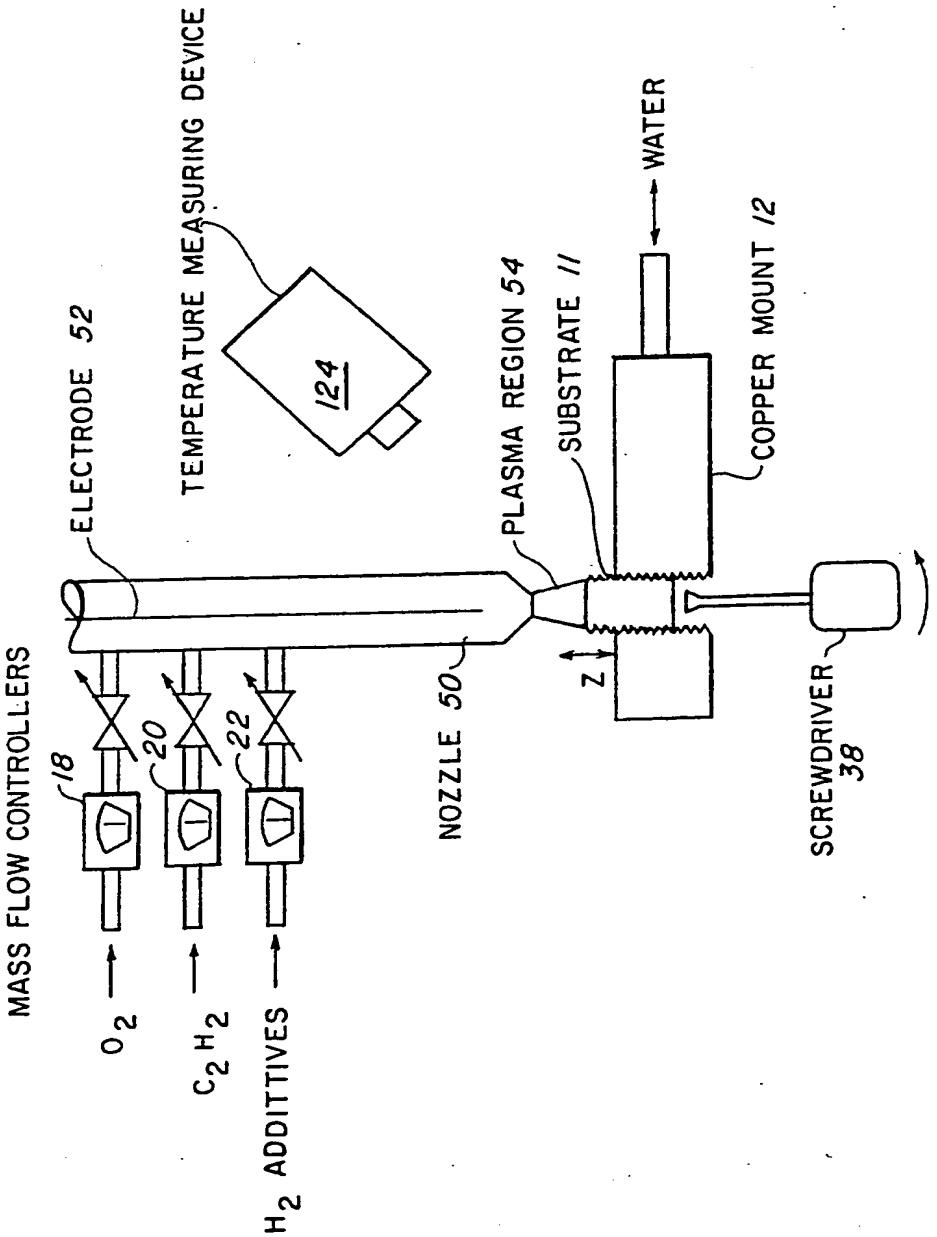
TEMPERATURE MEASURING DEVICE
124
ELECTRODE 52
PLASMA REGION 54
SUBSTRATE 11
WATER
COPPER MOUNT 12
MASS FLOW CONTROLLERS
18
20
22
NOZZLE 50
Z
SCREWDRIVER 38
O_2
C_2H_2
H_2 ADDITIVES

FIG. 8

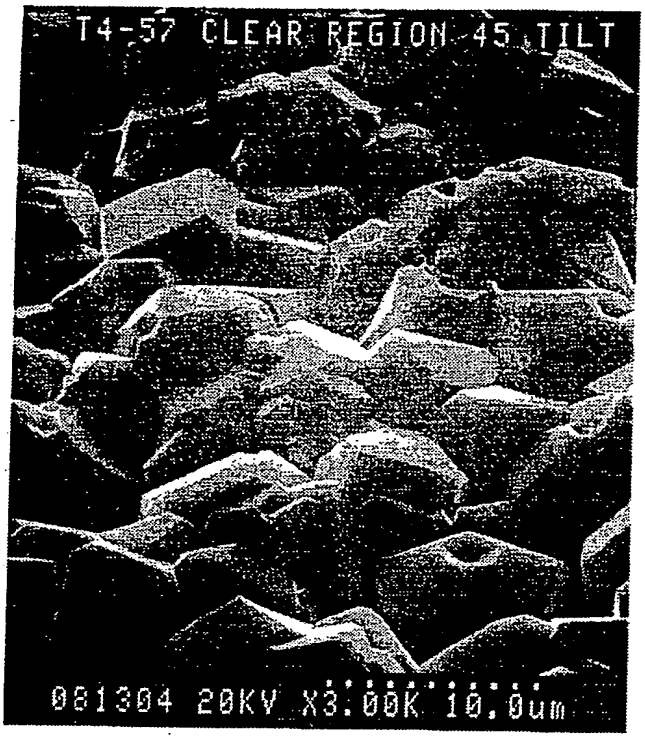

FIG. 9

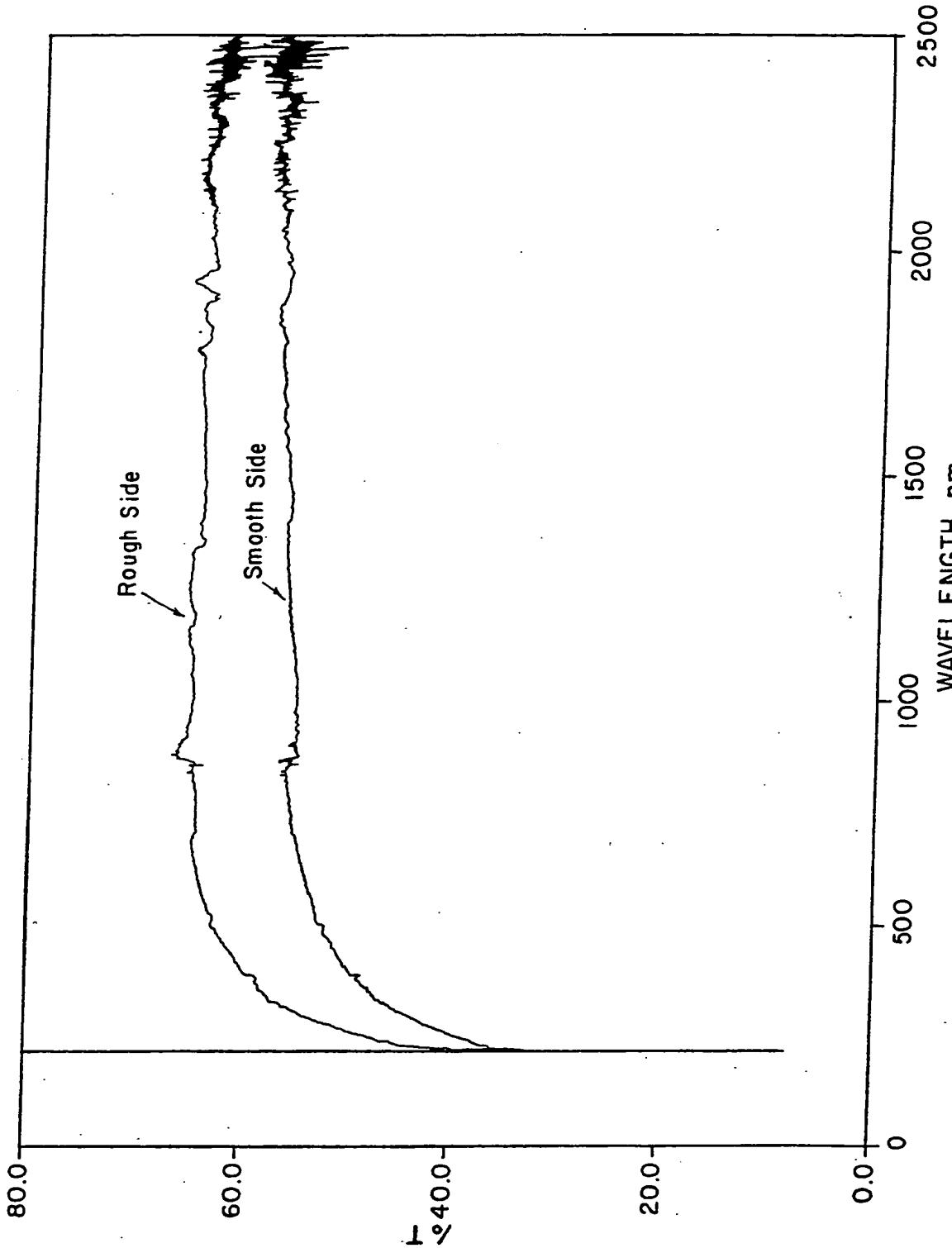
Rough Side
Smooth Side
80.0
60.0
40.0
20.0
0.0
T %
0
500
1000
1500
2000
2500
WAVELENGTH nm

FIG. 10

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/06787

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): C01B 31/06, C23C 16/26
US.CL: 423/446, 204/157.47, 427/249

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
US	423/249 427/249

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X,Y	US,A, 4,859493 (Lemelson) 22 August 1989, see column 21, lines 46-66.	1-3,11-12, 15,16,23,25,26
X,Y	US,A, 4,958,590 (Goforth) 25 September 1990, see column 1, lines 5-12.	1-3,11-19, 21-28
Y	US,A, 4,191,735 (Nelson et al) 4 March 1980, see column 1, lines 33-43.	21
X	Hansenn et al. "Diamond Synthesis Using an Oxygen-Acetylene Torch" Materials Letters, Vol. 7, No. 7, pp. 289-292, December 1988.	23-27
X	Hirose et al. "The Synthesis of High Quality Diamond in Combustion" pp 90-92.	23-28
A	EP,A 0,288,306 (Korihara et al), 12 October 1988, see entire document.	All
A	JP,A, 1.164,795 (Fujitsu LTD) 28 June 1989, see abstract	All

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13 December 1991	13 JAN 1992
International Searching Authority	**Signature of Authorized Officer**
ISA/US	Steve Kalinchak, Patent Examiner

Form PCT/ISA/210 (second sheet) (Rev.11-87)